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Influence of Land Use Land Cover on River Water Quality in Rural North Wales, UK

Elizabeth C. Crooks, Ian M. Harris, and Sopan D. Patil

Research Impact Statement: Our field study at two rural catchments in North Wales UK shows that the proportion of high-quality agricultural land in a catchment is one of the strongest predictors of its stream water quality.

ABSTRACT: Agricultural and rural land management practices can have a significant impact on the health of river ecosystems. In this study, our goal was to quantify the extent of land use influence on river water quality at two catchments in rural North Wales, Conwy and Clwyd. Stream water samples were collected bi-weekly from five sampling sites over a three-month period (September–November 2018) and analyzed in the laboratory to measure six water quality variables, namely, pH, electrical conductivity (EC), phosphorus, nitrate and ammonium concentrations, and bacterial coliform count. We then quantified their relationships with dominant land cover of the contributing catchments using two different land cover classification systems. Significant differences ($p < 0.05$) were observed across the sampling sites for pH, EC, nitrate and phosphorus concentration, and coliform count. Strong correlations were observed between pH and the proportion of Acid Grassland, and between nitrate levels and the proportion of Improved Grassland in the catchment. The presence of high-quality agricultural land correlated positively with nitrate and phosphorus concentrations and bacterial coliform count. Conversely, dominance of poor quality agricultural land correlated with lower levels of all the measured water quality indicators. Our results suggest that the proportion of high-quality agricultural land is a reliable indicator of stream water quality in rural catchments, most likely linked to intensive farming practices.

(KEYWORDS: water quality; land use land cover; agriculture; nonpoint source pollution; rural land management.)

INTRODUCTION

Maintaining good stream water quality in a catchment is often a challenging task due to the release of pollutants from both point and nonpoint sources (Baker 2005; Ongley et al. 2010; Zhou et al. 2016). Point sources of pollution, such as the outlets of wastewater treatment plants or combined sewer outflows, tend to be geographically confined and are relatively easy to identify and control (Lam et al. 2010; Wang et al. 2016). Nonpoint sources of pollution, on

the other hand, are much more difficult to characterize due to the complex and diffuse interaction between water runoff and landscape (Sliva and Dudley Williams 2001; Lam et al. 2010; Liu et al. 2016). The configuration and spatial extent of different land cover types within a catchment play an important role in determining the entry of nonpoint source pollutants into the stream (Basnyat et al. 2000; Giri and Qiu 2016; Liu et al. 2016).

Links between water quality and land use land cover have been studied in many parts of the world (Larned et al. 2004; Ahearn et al. 2005; Li et al.

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2008; Giri and Qiu 2016; Shi et al. 2017). Many of these studies have concluded that agricultural and urban are the two dominant land uses that strongly correlate with poorer water quality. Agricultural land use has been associated with higher levels of nitrogen, phosphorus, and sediment load (Johnson et al. 1997; Smart et al. 1998; Arheimer and Lidén 2000), whereas the urban land use has been shown to increase total suspended solids, ammonium, and acidity in the streams (Ahearn et al. 2005; Clinton and Vose 2006; Peters 2009). Larned et al. (2004) studied water quality in the low elevation streams of New Zealand and found that *Escherichia coli* and dissolved nitrogen and phosphorus concentrations were two to seven times higher in the pastoral and urban land classes compared to the native and plantation forest classes. Ahearn et al. (2005) correlated water quality with land use land cover at the Cosumnes watershed in California. They found that both agricultural area and population density correlated well with total suspended solids but there was a lack of correlation between population density and nitrate loading. In China, Li et al. (2008) analyzed water quality data from 42 sampling sites in the upper Han River Basin. They showed that the percentage of urban area was a good predictor of pH and dissolved phosphorus, whereas the agricultural land was a good predictor of suspended particulate matter and potassium.

In addition to land use land cover, hydrological variation in a catchment is also known to have a substantial impact on stream water quality (Johnes 1996; Johnes and Heathwaite 1997; Walter et al. 2000; Bu et al. 2014). For instance, Watson et al. (2000) studied nutrient transport from grazed grassland areas in Northern Ireland and found that the loss of nitrates was the highest after a dry summer. Crowther et al. (2002) quantified fecal-indicator concentrations at two lowland pastoral catchments in the United Kingdom and showed ten-fold increase in fecal coliform in the stream water at high flows compared to low flows. Nonetheless, they also found that poor water quality at high flows was positively correlated with land use/management variables associated with intensive livestock farming. Shi et al. (2017) analyzed long-term water quality data at the Dan River Basin in China and found that electrical conductivity (EC), concentrations of nitrate and ammonium, and suspended solids tend to be higher in the wet season, whereas biological oxygen demand, chemical oxygen demand, and dissolved oxygen tend to be higher in the dry season.

In United Kingdom, water quality is a growing concern as nutrient levels in freshwater, riverside sediment and wetlands have increased substantially in recent decades and have caused eutrophication and

ecological decline in many parts of the country (Haygarth and Jarvis 2002; Mainstone and Parr 2002). Agricultural pollution incidents almost doubled in England and Wales in the period from 1978 to 1985, which first raised the issue of river health across the United Kingdom (Merrington et al. 2002). Excess nutrients from agricultural land are the major cause of elevated phosphorus, nitrate and ammonium concentrations in the surface waters of the United Kingdom (Parker 1991). Rural areas with higher density of livestock farming, like North Wales, are also vulnerable to the pollution from bacterial coliforms entering the streams (Edwards et al. 2008; Williams et al. 2012). Although the management of river basins in the United Kingdom increasingly involves attention to land use and land management (Newson 1991), pinpointing a direct pollutant that is causing riverine ecosystem stress and tracing its source is difficult due to the large number of factors that can affect stream water quality (Sliva and Dudley Williams 2001; Baker 2005; Giri and Qiu 2016). Weatherhead and Howden (2009) suggest that a clearer distinction needs to be made between land use and land management, as water quality concerns might often be more directly related to land management practices than to land uses. Thus, while knowing the spatial distribution of land cover or habitat classes (e.g., grassland, woodland, urban) in a catchment is certainly useful to characterize the broader controls on stream water quality, relying solely on this information is unlikely to provide a full understanding of the influencing factors.

In this study, we seek to quantify the extent of land use influence on water quality in rural catchments using two different land cover classification systems. Specifically, the first land classification system focuses on characterizing the broad habitat types on the landscape (e.g., coniferous woodland, arable land, improved grassland), whereas the second classification focuses on characterizing the potential productivity and thus varying intensities of agricultural use. Our two study catchments in North Wales, Conwy and Clwyd, form an interesting case study as they are adjacent to each other, have large drainage areas ($>500 \text{ km}^2$) and low population densities, and are dominated by similar agricultural activities. However, agricultural activities in the Conwy catchment, based around grassland and livestock production (predominantly sheep with some beef enterprises) occur on a poorer quality and less productive land. The Clwyd catchment, on the other hand, contains a larger proportion of high productive land types and can support these agricultural activities with more intensive land management. While previous studies have identified links between land use and water quality variables in parts of the Conwy catchment (Williams et al. 2012; Cooper et al. 2014), a direct comparison of these catchments, in the context of

similar land use but of differing intensity, has not yet been undertaken. We collected water samples from five sampling sites across these two catchments at a bi-weekly frequency over a three-month period (September–November 2018). Water samples were analyzed in the laboratory to measure six water quality variables: pH, EC, phosphorus, nitrate and ammonium concentrations, and bacterial coliform count. The relationships of these water quality variables with dominant land use land cover of the contributing catchments were then quantified using the two different but complementary land cover classification systems.

MATERIALS AND METHODS

Study Sites

Our research was undertaken in the Conwy and Clwyd catchments in North Wales, United Kingdom,

with two stream sampling sites in Conwy and three in Clwyd (Figure 1). The total drainage area of Conwy and Clwyd catchments is 564 and 803 km², respectively (Dallison et al. 2020). These two catchments are in close geographic proximity, both flow northwards to drain into the Irish Sea, and experience similar weather conditions in the same time-frame. Sample sites for the Conwy Catchment are situated at Penmachno (henceforth referred to as Site 1 CO; location: 53.0406°N, 3.8059°W) and Llanrwsst (Site 2 CO; location: 53.1446°N, 3.8041°W). Clwyd sample sites are situated at Ruthin (Site 1 CW; location: 53.1413°N, 3.3072°W), Abergele (Site 2 CW; location: 53.2333°N, 3.5747°W), and Rhuddlan (Site 3 CW; location: 53.2912°N, 3.4685°W). Our sample sites were chosen using the following criteria: (1) they should be easy to access, (2) all sites can be visited and sampled in a single day using a motor vehicle, and (3) no access permit is required to enter the sample site through private property. Note that the Site 1 CO catchment is a subcatchment of the Site 2 CO catchment. Similarly, the Site 1 CW and Site 2 CW

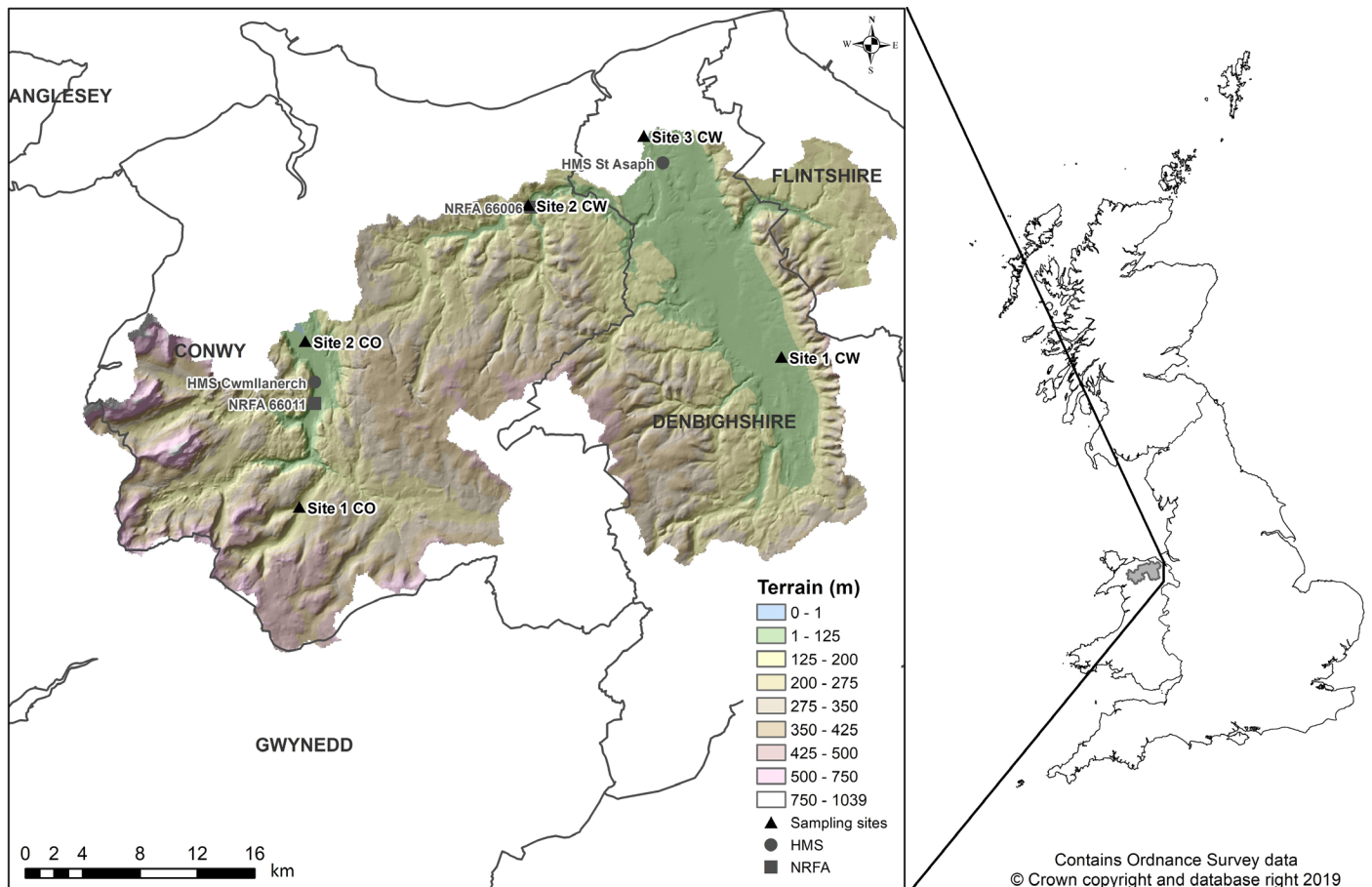


FIGURE 1. Location map of the five stream sampling sites, two Harmonized Monitoring Scheme (HMS) sites (Cwmllanerch and St Asaph), and two National River Flow Archive (NRFA) streamflow gauging stations (66011 Conwy at Cwmllanerch and 66006 Elwy at Pont-y-Gwyddel). CO = Conwy; CW = Clwyd.

catchments are subcatchments of the larger Site 3 CW catchment (see Figure 2).

Average annual precipitation in our study region varies from 2,000 mm in the western parts of the Conwy catchment (Cooper et al. 2014) to 950 mm in the eastern parts of the Clwyd catchment (Dallison et al. 2020), primarily due to the rain-shadow effect created by the Snowdonia Mountain Range that is located to the west of Conwy. Air temperature in the region typically ranges between 3°C in the winter and 19°C in the summer. Total population in our study region is just under 49,000 (mean = 40.5 residents per km²) as outlined in the 2011 census data (Reis et al. 2017), with Conwy being more sparsely populated than Clwyd. Major population areas in the Conwy catchment are Llanrwst and Betws-Y-Coed, and in the Clwyd catchment are St Asaph, Denbigh, and Ruthin. Agricultural activities in the Conwy catchment, especially in its headwater regions, are based around grassland and livestock production, predominantly sheep, with some beef enterprises

largely involving suckler cow herds. In contrast, the Clwyd catchment contains a broader range of agricultural enterprises which, in addition to the ones already listed for Conwy, include intensive dairying, growing forage maize, cereal, and limited horticultural crops.

Land Use Land Cover Datasets

Two different datasets were used to characterize the land cover of the catchments that drain toward each sampling site. Figure 2 shows the land cover map that was created using the Centre for Ecology and Hydrology's (CEH) UK Land Cover Map 2015 (LCM 2015) (Rowland et al. 2017), which contains the data derived from satellite images and is based on UK Biodiversity Action Plan Broad Habitats classes. LCM 2015 classifies UK land cover into 21 different categories, with classes such as broadleaved woodland, improved grassland, bog, saltmarsh, etc.

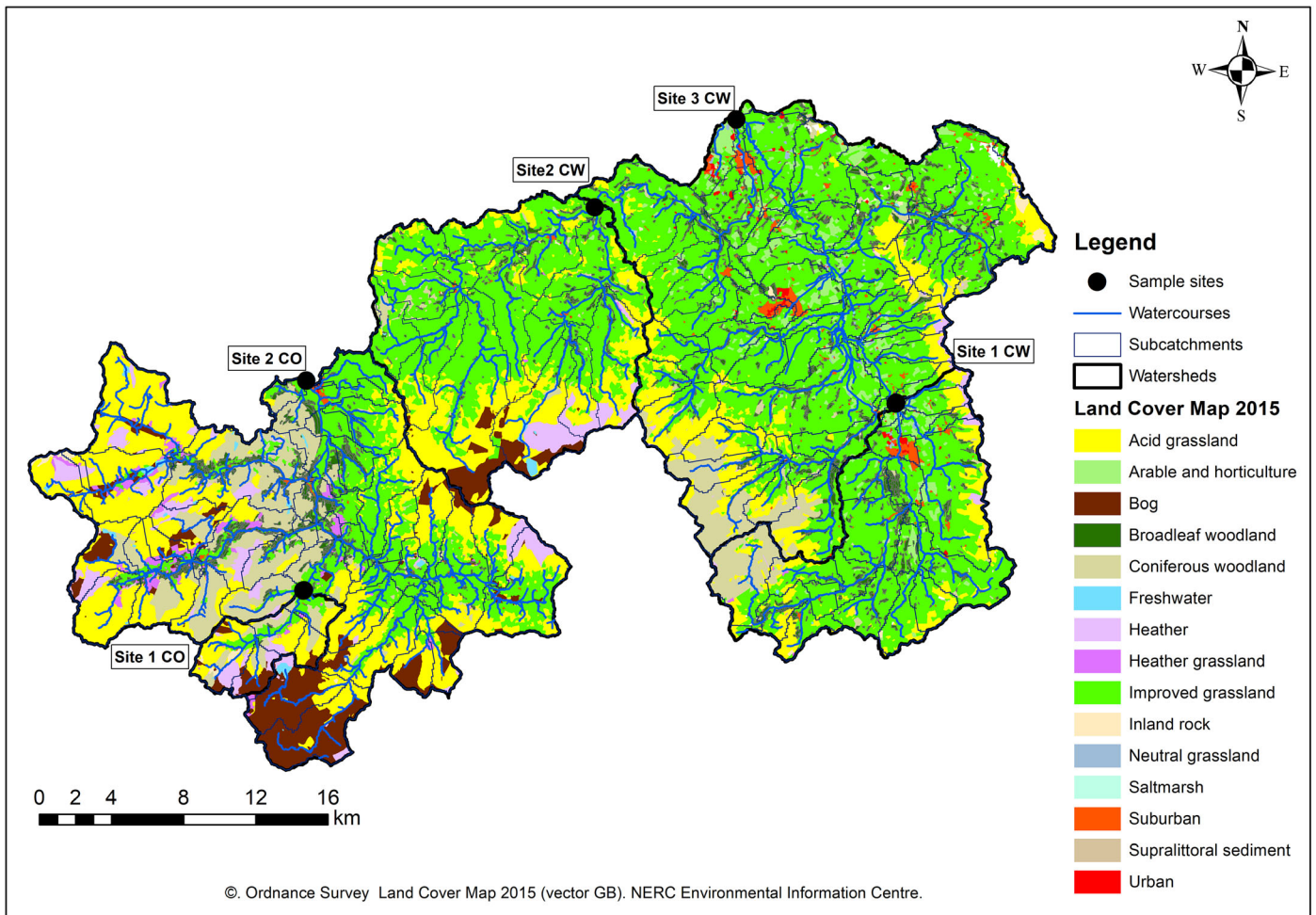


FIGURE 2. Land cover map of the catchments contributing to our five sampling sites using the Land Cover Map 2015 (LCM 2015) land classification system.

Figure 3 shows the LCM that was created using the predictive Agricultural Land Cover (pALC) dataset (MAFF 1988). This dataset is based on the principles of the Agricultural Land Classification System of England & Wales, and the Revised Guidelines and Criteria for Grading the Quality of Agricultural Land. pALC classifies the land into five grades, with Grade 1 being the best quality land for agricultural use and Grade 5 being the worst. National planning policy in England and Wales defines Grade 1, 2, and 3a land to be the most versatile agricultural land and these are often subject to intensive farming practices (MAFF 1988). Land with Grades 4 and 5 is considered to have severe limitations for agriculture and is often restricted to be used as permanent pasture or rough grazing land.

The areal coverage data of each land cover class in the catchments that drain toward our five sample sites are presented in Appendix (using both LCM 2015 and pALC data). In addition, Tables A1–A5 of

Appendix also present the land cover class distribution from LCM 2007, which was the previous version of the LCM 2015 database and for which the land cover classification was conducted using the 2007 data. A comparison of land cover class distribution between the LCM 2007 and LCM 2015 databases shows minor land cover changes. Thus, even though there is a slight temporal mismatch in the LCM 2015 land cover map and our water quality sampling (conducted in 2018), the land use land cover in Conwy and Clwyd river basins has been stable over the last decade.

Acid Grassland is the dominant land cover in the catchments of both Conwy sites (~35%), whereas Improved Grassland is the dominant land cover in the catchments of all three Clwyd sites (~60%). In terms of agricultural land quality, the Conwy site catchments almost entirely consist of the poorer Grade 4 and Grade 5 land, which is 88.7% for Site 1 CO and 77.9% for Site 2 CO. The Clwyd site

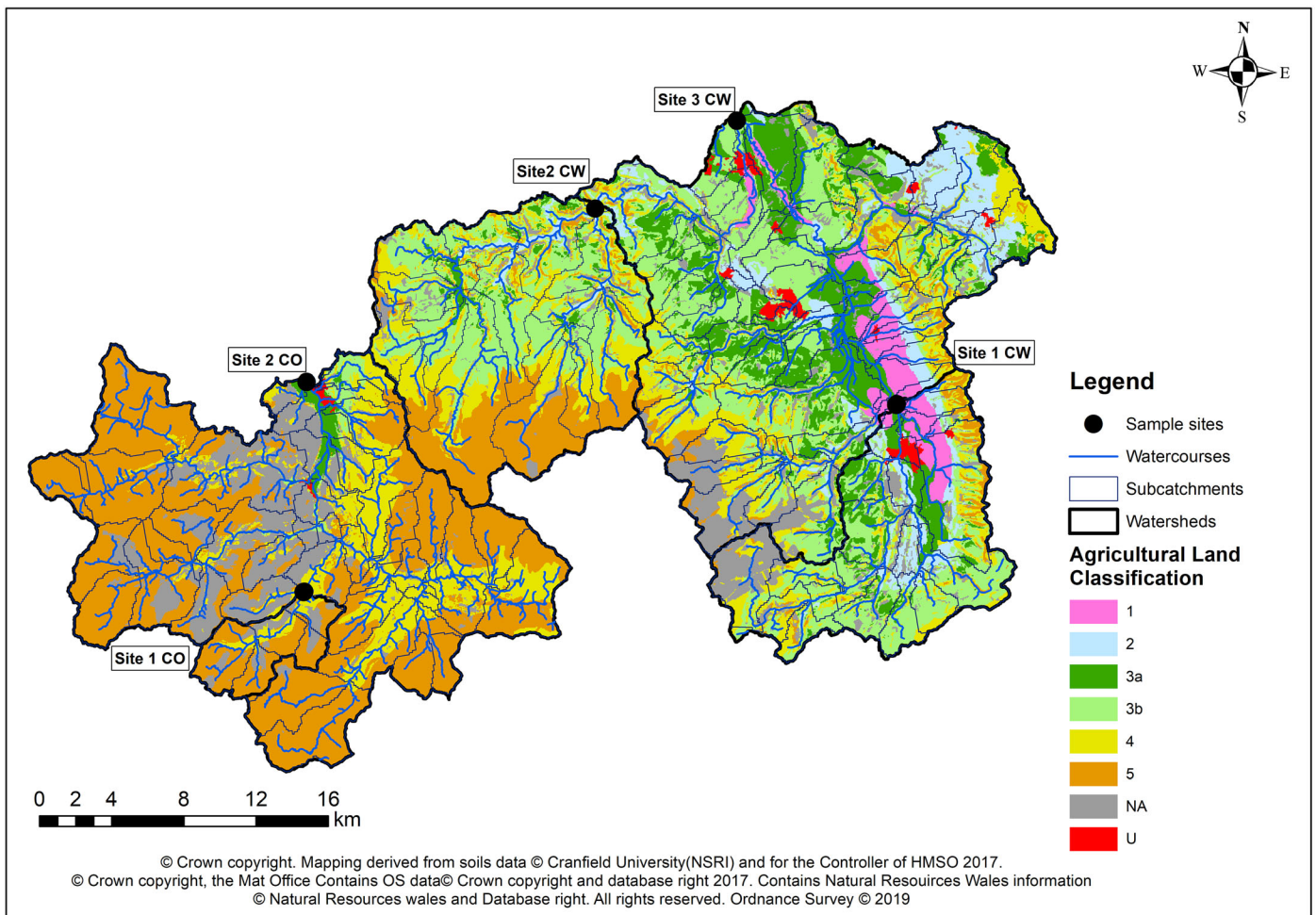


FIGURE 3. Land cover map of the catchments contributing to our five sampling sites using the predictive Agricultural Land Cover (pALC) land classification system. Numbers 1–5 denote the land quality as classified by pALC, NA is the nonagricultural land, and U is urban land use.

catchments contain a sizable proportion of Grade 4 and 5 land, with 20.46% for Site 1 CW, 52.88% for Site 2 CW, and 29.66% for Site 3 CW. Nonetheless, they also contain a good amount of high-quality agricultural land, i.e., with Grades 1, 2, and 3a (29.58% for Site 1 CW, 6.99% for Site 2 CW, and 26.78% for Site 3 CW). Soils in the Conwy catchment are predominantly loamy and clayey floodplain soils, with an underlying geology that is dominated by Permo-Triassic sandstones, with some igneous rocks and slate (Simpson et al. 1993; Williams et al. 2012; Cooper et al. 2014). Conversely, the Clwyd catchment predominantly contains stoneless silty clay loam soil, of which a high percentage has been adapted for agricultural use, with similar geology to the Conwy catchment (Simpson et al. 1993).

Water Quality Data Collection

Field samples were collected over a three-month period, with instream water samples taken from our five sampling sites at a bi-weekly time interval (September 23, 2018, October 7, 2018, October 21, 2018, November 11, 2018, and November 25, 2018). Average daytime temperature during the sampling period was 10°C–15°C. On all five sampling days, we took three water samples at each sampling site, which were then tested for pH, EC, nitrate, phosphorus, ammonium, and bacterial coliforms. The values of water quality variables we report in the Results section are the average values from the three water samples at each study site.

pH and EC levels of the water samples were measured using the calibrated HANNA pH and EC instruments. Nitrate, ammonium and phosphorus concentrations in the water samples were tested using 96 well plates, against six standards per pollutant. Both ammonium and nitrate determination can be performed by the extraction of potassium chloride. Nitrate (NO_3) tests consisted of placing 100 μL of each standard or sample into a separate well, followed by 100 μL of Vanadium(III) chloride (VCl_3), 50 μL of N-(1-Naphthyl)ethylenediamine dihydrochloride, and 50 μL of Sulfanilamide and mix. After 15–20 min at room temperature, absorbance rates read at 540 nm on a BioTek microplate-reader. The ammonium test was completed similarly, as 150 μL of standard or sample was placed in each well of the micro plate, followed by 15 μL of Ethylenediaminetetraacetic acid, 60 μL of Na-salicylate-nitroprusside reagent, and 30 μL of hypochlorite reagent, then mixed. Samples were incubated at 37°C for 30 min, then absorbance was read at 667 nm. In the Results section, we have reported the concentrations of nitrate and ammonium in their

molecular form. Phosphorus analysis consisted of 221 μL of sample or standards pipetted into a well, with 40 μL of Ames reagent (Murphy and Riley 1962), and absorbance was read at 880 nm. To test for bacterial coliforms, a 30 mL water sample from each site visit was filtered through a cellulose nitrate filter and placed on a chromogenic agar plate and incubated overnight at 37°C. Bacterial colonies were then observed on the UTI media through a suspended magnifying glass. Colonies observed included *Enterobacter aerogenes*, *Enterococcus faecalis*, *E. coli*, *Proteus mirabilis*, and *Staphylococcus/Staphylococcus aureus*.

Data Analysis

To quantify the spatial and temporal variability in the water quality variables, we conducted a series of one-way analysis of variance (ANOVA) tests. Water quality variables were grouped by sites to characterize the spatial variability and by sampling days to characterize the temporal variability. For variables that showed significant differences in the mean values through ANOVA, post hoc tests were conducted. Specifically, we used multiple paired *t*-tests with Bonferroni correction (Sedgwick 2012) to further characterize the variability among the sites or sampling days. To quantify the influence of land use land cover on instream water quality, we calculated the Spearman Rank Correlation (Gauthier 2001) between the measured water quality variables and the percentage area covered by selected land cover types. Spearman Rank correlation was specifically used to characterize the increasing/decreasing trend of these relationships and their strength. The formula for Spearman's Rank correlation (ρ) is as follows:

$$\rho = 1 - \frac{6 \cdot \sum d^2}{M \cdot (M^2 - 1)} \quad (1)$$

where, d is the difference between the ranks of each observation on the two variables under consideration, and M is the total number of observation points. Spearman's ρ varies from -1 to $+1$, with -1 being a perfect monotonically decreasing relationship and $+1$ being a perfect monotonically increasing one. Significance of the ANOVA tests and Spearman Rank Correlation was tested at both 95% ($p < 0.05$) and 99% ($p < 0.01$) confidence levels, whereas the significance of post hoc *t*-tests was tested only at 95% confidence level.

Prior to the correlation calculation, measurements of all six water quality variables were averaged across the sampling days at each site. Selection of the

land cover types for correlation calculation was done as follows. For the pALC classification, we created two land groups, Good Agricultural Land (GAL) consisting of Grades 1, 2, and 3a and Poor Agricultural Land (PAL) consisting of Grades 4 and 5. This grouping is consistent with the National planning policy in England and Wales, which considers the GAL grades to be suitable for a wide range of agricultural activities and the PAL grades to be of limited agricultural use (MAFF 1988). For the LCM 2015 classification, we chose only those land cover classes that cover more than 10% area of at least one of the sample site catchments. The 10% areal coverage threshold was used to ensure that our analysis was not severely affected by any accuracy issues in the land cover classification system, which are more likely to have an impact on land cover classes with low areal coverage. This condition limited our selection to Improved Grassland, Acid Grassland, Bog, and Woodland (broadleaf + coniferous). Below, we provide a brief description of these four land cover types, as outlined by the UK Biodiversity Action Plan. Improved Grasslands are characterized by vegetation dominated by fast-growing grasses on fertile, neutral soils and are typically either managed as pasture or mown regularly for silage production. Acid Grasslands are dominated by grasses on a range of lime-deficient soils which have been derived from acidic bedrock or from superficial deposits such as sands and gravels (soil pH < 5.5). Bogs are wetlands that support peat forming vegetation and which receive mineral nutrients principally from precipitation rather than from ground water. Common vegetation in a bog includes ericaceous, herbaceous and mossy swards in areas with a peat depth >0.5 m. Woodlands, both broadleaf and coniferous, are characterized by vegetation dominated by trees >5 m high when mature and a canopy cover of >20%. Broadleaved woodlands include stands of both native and non-native broadleaved trees and yew; whereas coniferous woodlands include semi-natural stands and plantations of both native and non-native coniferous trees.

Validation with External Data

Given that our water sample collection was limited to only five days in the autumn of 2018, we sought to enhance our analysis by further using: (1) streamflow data from nearby stream gauge locations, and (2) historical water quality data collected by the UK's Environment Agency (EA) at locations near our sample sites. Daily streamflow data for the calendar year 2018 were obtained from CEH's National River Flow Archive (NRFA; <https://nrfa.ce>

h.ac.uk) and was available at only two locations in our study region (see Figure 1), Conwy at Cwmllanerch (NRFA 66011; near Site 2 CO) and Elwy at Pont-y-Gwyddel (NRFA 66006; near Site 2 CW). While streamflow data were not used directly to quantify or correlate any relationships, we did utilize it to improve the interpretation of our water quality results.

Historical water quality data were obtained from EA's Harmonized Monitoring Scheme (HMS) dataset and were available from 2010 to 2013 at only two sites in our study region (see Figure 1), Conwy at Cwmllanerch (HMS Cwmllanerch; near Site 2 CO) and Clwyd at St Asaph (HMS St Asaph; near Site 3 CW). The available water quality variables at these sites included: pH (51 samples at Cwmllanerch, 47 samples at St Asaph), and EC and nitrate concentration (50 samples of each at Cwmllanerch, 48 samples of each at St Asaph). Note that, unlike the water quality data that we collected for this study, the HMS data contain water quality samples collected across every month of the year between 2010 and 2013 and a wider range of hydrological conditions. HMS water quality data were used to determine how the absolute values and variability in our field collected 2018 data compared with a larger historical dataset.

RESULTS

Tables 1–6 show the measurements of our six water quality variables, pH, EC (S/m), nitrate concentration (mg/L), phosphorus concentration (mg/L), ammonium concentration (mg/L), and bacterial coliform count, respectively, across the five sampling sites and five sampling days. Overall, these measurements show that water quality in the Conwy sites is better than in the Clwyd sites in terms of EC, Nitrate, Phosphorus, and bacterial coliform count. Across the sampling period, Clwyd sites had higher water pH levels, with Site 3 CW having the highest pH most of the time (Table 1). Site 3 CW also had the highest average water EC throughout the sampling period (Table 2). The highest nitrate concentration was recorded at Site 1 CW, with Site 3 CW not far behind (Table 3). The two Conwy sites recorded very low (barely detectable) nitrate concentrations. For phosphorus concentration, Site 3 CW recorded the highest average levels, mainly due to the high levels detected in the 21 October sample (Table 4). The lowest phosphorus levels were recorded at Site 1 CO, followed closely by Site 2 CW. Ammonium concentration levels were low across all five sites for most of the

sampling period, except at Site 3 CW on 21 October (Table 5). The cause for this high reading is not entirely certain, but we suspect that it might have been caused by an anomalous pollutant release event near that site on the sampling day, which is also detected in the high phosphorus level but not in the nitrate level. Bacterial coliform counts were higher at the Clwyd sample sites than at the Conwy sample sites (Table 6). Site 1 CO saw consistently low levels of bacterial coliforms, whereas Site 3 CW had a coliform count that kept increasing through the sampling period. None of the Clwyd sample sites had a coliform count of below 100.

Figure 4 shows the comparison of our water quality data, collected in autumn 2018, with the historical HMS water quality data. Although the HMS data can only be compared at two sample sites (Site 2 CO and Site 3 CW) and for three variables (pH, EC, and nitrate concentration), it still constitutes an

TABLE 1. pH measurements at all five sample sites.

Date	Site 1 CO	Site 2 CO	Site 1 CW	Site 2 CW	Site 3 CW
23-Sep	7.11	7.49	8.90	7.82	8.68
07-Oct	6.56	6.89	7.69	7.13	7.38
21-Oct	6.75	6.90	9.03	8.44	8.22
11-Nov	8.51	6.84	6.77	7.51	8.54
25-Nov	6.84	7.04	8.39	7.87	7.64
Average	7.15	7.03	8.16	7.75	8.09

TABLE 2. Electrical conductivity (EC) measurements (S/m) at all five sample sites.

Date	Site 1 CO	Site 2 CO	Site 1 CW	Site 2 CW	Site 3 CW
23-Sep	38.8	94.7	214.7	93.2	934.3
07-Oct	33.0	60.6	444.7	108.5	906.0
21-Oct	41.9	60.4	247.0	105.1	736.3
11-Nov	27.4	32.5	366.9	118.5	286.8
25-Nov	28.6	68.8	150.6	98.4	274.2
Average	34.0	63.4	284.8	104.8	627.5

TABLE 3. Nitrate concentration levels (mg/L) at all five sample sites.

Date	Site 1 CO	Site 2 CO	Site 1 CW	Site 2 CW	Site 3 CW
23-Sep	0.49	0.52	1.39	0.92	2.19
07-Oct	0.34	0.43	1.17	0.66	1.40
21-Oct	0.36	0.55	1.68	0.56	0.90
11-Nov	0.41	0.45	1.48	0.85	1.48
25-Nov	0.50	0.37	1.81	0.81	1.53
Average	0.42	0.46	0.76	0.76	1.50

TABLE 4. Phosphorus concentration levels (mg/L) at all five sample sites.

Date	Site 1 CO	Site 2 CO	Site 1 CW	Site 2 CW	Site 3 CW
23-Sep	0.62	0.57	1.15	0.58	1.68
07-Oct	0.58	0.59	2.24	0.59	1.35
21-Oct	0.59	0.63	1.25	0.61	5.36
11-Nov	0.59	0.59	0.97	0.62	0.83
25-Nov	0.58	0.84	0.82	0.59	1.55
Average	0.59	0.65	1.29	0.60	2.15

TABLE 5. Ammonium concentration levels (mg/L) at all five sample sites.

Date	Site 1 CO	Site 2 CO	Site 1 CW	Site 2 CW	Site 3 CW
23-Sep	0.28	0.28	0.29	0.28	0.40
07-Oct	0.29	0.28	0.27	0.31	0.28
21-Oct	0.28	0.27	0.30	0.30	5.74
11-Nov	0.28	0.29	0.29	0.29	0.30
25-Nov	0.28	0.28	0.30	0.31	0.36
Average	0.28	0.28	0.29	0.30	1.42

important comparative benchmark for our field sampled data. First, a comparison of the HMS data between the Cwmllanerch and St Asaph sites shows that, even after accounting for multiyear hydrological variations (2010 to 2013), the water quality is better at Cwmllanerch. This is consistent with our sampling data, which shows better water quality at the Conwy sites compared to the Clwyd sites. pH values range from 5.25 to 7.51 (median = 6.73) at Cwmllanerch and from 7.01 to 8.42 (median = 7.98) at St Asaph. EC values range from 36 to 111 S/m (median = 69.5 S/m) at Cwmllanerch and from 289 to 534.4 S/m (median = 409.5 S/m) at St Asaph. Nitrate concentration ranges from 0.196 to 1.73 mg/L (median = 0.41 mg/L) at Cwmllanerch and from 2.3 to 4.7 mg/L (median = 3.73 mg/L) at St Asaph. A comparison between Cwmllanerch and Site 2 CO shows that most of our sample data falls within the range of the historical HMS data (Figure 4a, 4c, and 4e). However, this does not seem to be the case when comparing St Asaph and Site 3 CW (Figure 4b, 4d, and 4f). The variability in pH and EC values is much higher in our Site 3 CW data and supersedes the variation in the HMS St Asaph data, whereas the nitrate concentration at Site 3 CW is substantially lower than at St Asaph.

Figure 5 shows the daily streamflow data for calendar year 2018 at two stream gauge stations, NRFA 66011 (Conwy at Cwmllanerch) and NRFA 66006 (Elwy at Pont-y-Gwyddel), and also highlights the streamflow values on our water sampling days. At

TABLE 6. Bacterial coliform count at all five sample sites. Note that no measurement was available for the 21-Oct due to sample contamination.

Date	Site 1 CO	Site 2 CO	Site 1 CW	Site 2 CW	Site 3 CW
23-Sep	21	90	211	123	115
07-Oct	14	75	103	110	116
21-Oct	21	38	216	141	N/A
11-Nov	32	117	334	462	285
25-Nov	14	50	182	120	375
Average	20	74	209	191	222

both locations, our first sampling day occurred just after the first big hydrological events of the autumn season. The second, third, and fifth sampling days occurred during the periods of relatively low flows. The fourth sampling day had the highest flow values, compared to other four days, for both locations. Table 7 shows the actual streamflow values, in m^3/s , and their percentile value among the 2018 flows. Although limited in number (only 5), our sampling days were spread across a wide range of hydrological flow conditions, from 23rd to 85th percentile for Conwy at Cwmllanerch and 35th to 79th percentile for Elwy at Pont-y-Gwyddel.

For all six water quality variables, the temporal ANOVA test, with samples grouped by sampling day, showed no significant differences ($p > 0.05$) in the measurements across the sampling days. Spatial ANOVA test, with samples grouped by sample site, showed significant differences in the measurements across the sample sites for all variables except ammonium concentration. ANOVA tests for pH, EC, and nitrate concentration were significant at 99% confidence level ($p < 0.01$), whereas the tests for phosphorus concentration and bacterial coliform count were only significant at 95% confidence level ($0.01 < p < 0.05$). Post hoc t -tests showed significant differences (adjusted $p < 0.05$) in the pH levels between Site 1 CO and Site 1 CW, Site 1 CO and Site 3 CW, and Site 2 CO and all three CW sites. Differences in EC were found to be significant across all the sampling site pairs. Nitrate concentration levels were significantly different across all the sampling site pairs, except for between Site 1 CO and Site 2 CO, and Site 1 CW and Site 3 CW. Although the ANOVA test showed significant inter-site differences in phosphorus concentration (albeit only at 95% confidence level), no significant differences were detected across sample site pairs in the post hoc tests. For bacterial coliform count, significant differences were found between Site 1 CO and

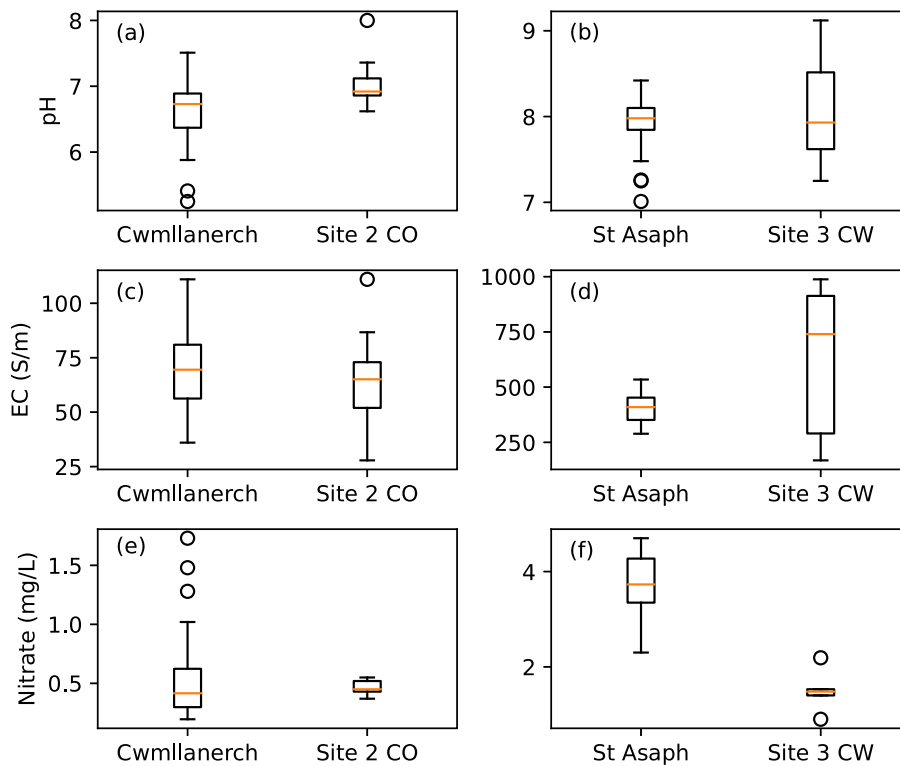


FIGURE 4. Comparison between the historical HMS data and our field sample data for pH (a,b), EC (c,d), and nitrate concentration (e,f). HMS sample location at Cwmllanerch is compared with Site 2 CO (a, c, and e), whereas the HMS sample location at St Asaph is compared with Site 3 CW (b, d, and f).

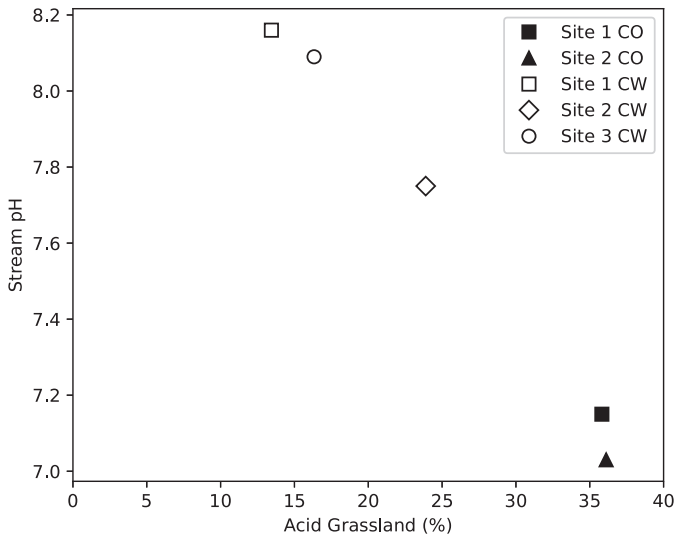


FIGURE 6. Relationship between the proportion of Acid Grassland land cover in a catchment and stream pH.

Site 2 CO, Site 1 CO and Site 1 CW, Site 1 CO and Site 3 CO, and Site 2 CO and Site 1 CW.

Table 8 shows the Spearman Rank Correlation (ρ) between the six water quality variables and percentage areal coverage of selected land cover types (see Data Analysis section for details on how the land cover types were selected). For pH, a strong negative correlation was observed with Acid Grassland ($p < 0.01$), suggesting that catchments with higher proportion of Acid Grassland will have lower stream pH. Figure 6 shows pH measurements plotted against the percentage area of Acid Grassland. pH levels of the two Conwy sites are much lower than the Clwyd sites. Similar, but weaker, negative correlations for pH were obtained with bog and PAL land covers ($0.01 < p < 0.05$). For EC, no strong correlation ($p < 0.01$) was observed with any land cover type. Nonetheless, positive correlations were obtained with Improved Grassland and GAL and negative correlations with bog and PAL ($0.01 < p < 0.05$).

Nitrate concentration showed strong positive correlation ($p < 0.01$) with Improved Grassland and GAL and strong negative correlation with bog and PAL. Figure 7a shows the relationship between

nitrate concentration and the percentage area of GAL, which clearly demonstrates that catchments with higher proportion of GAL have far higher nitrate levels in their streams. Phosphorus concentration did not have any significant correlation with the selected land cover types. Nonetheless, a positive relationship does exist between phosphorus concentration and the proportion of GAL in a catchment (see Figure 7b). Catchments with higher proportion of GAL did contain more phosphorus, but there was a big difference in the levels among the two most dominant agricultural catchments (Site 1 CW and Site 3 CW). This difference could potentially be attributed farm level differences in the agricultural practices in these catchments. Ammonium concentrations showed significant negative correlation only with Woodland land cover. However, Figure 8 shows that the ammonium levels at only one site (Site 3 CW) are anomalously higher. At all other sites, hardly any ammonium concentration was detected. Bacterial coliform count showed significant positive correlations ($0.01 < p < 0.05$) with Improved Grassland and GAL and negative correlations with bog and PAL. Figure 9 shows the relationship between coliform count and percentage area of Improved Grassland. All three Clwyd sites, which have a much higher proportion of Improved Grassland compared to the Conwy sites, show a much higher instream presence of bacterial coliform.

DISCUSSION

The EC and pH levels of a watercourse are important indicators of river quality and health. They not only influence the water chemistry, microbial activity and fish health (Kroglund et al. 2008), but also the salinity and nutrient availability/uptake. EC measurements were higher in the Clwyd sites compared to the Conwy sites. Moreover, this pattern is consistent with the historical HMS data (Figure 4), which shows that the EC values at St Asaph (in Clwyd) are much higher than those at Cwmllanerch (in Conwy).

TABLE 7. Streamflow and their respective 2018 percentile values for our five sampling days at NRFA 66011 (CO at Cwmllanerch) and NRFA 66006 (Elwy at Pont-y-Gwyddel).

Date	NRFA 66011 Flow (m ³ /s)	NRFA 66011 percentile value for 2018	NRFA 66006 Flow (m ³ /s)	NRFA 66006 percentile value for 2018
23-Sep	17.04	70.2	2.769	52.7
07-Oct	6.906	44	1.051	35
21-Oct	5.441	35.5	2.373	50
11-Nov	31.68	85.2	6.717	79.2
25-Nov	3.739	23.2	1.765	42.6

TABLE 8. Spearman Rank Correlation (ρ) of all six water quality variables with selected land cover types.

Land cover	pH	EC	Nitrate	Phosphorus	Ammonium	Coliform
Acid grassland	-1	-0.8	-0.9 ¹	-0.6	-0.7	-0.8
Improved grassland	0.9 ¹	0.9 ¹	1	0.8	0.6	0.9 ¹
Bog	-0.9 ¹	-0.9 ¹	-1	-0.8	-0.6	-0.9 ¹
Woodland	-0.6	-0.6	-0.5	-0.2	-0.9 ¹	-0.6
GAL	0.9 ¹	0.9 ¹	1	0.8	0.6	0.9 ¹
PAL	-0.9 ¹	-0.9 ¹	-1	-0.8	-0.6	-0.9 ¹

Note: Bold value indicates 99% significance level.

GAL, Good Agricultural Land; PAL, Poor Agricultural Land.

¹95% significance level.

Nonetheless, measurements at one site, Site 3 CW, were significantly higher than all other sites during our sampling period. We suspect that the high EC levels at Site 3 CW are unlikely to be due to the land cover of its contributing catchment, given that its distribution of major land cover types is quite similar to the Site 1 CW catchment. Among all our sample sites, Site 3 CW is located closest to the sea (Figure 1), only three kilometers away from the mouth of the river, and could possibly be influenced by the tidal flows. The EC levels obtained at Site 3 CW are comparable with those from tidally influenced watercourses (Harris 2009). Overall, our results suggest that upstream land use land cover does not have a large influence on the EC levels at any of our study sites.

Throughout the sampling period, stream pH levels were considerably lower at the Conwy sites than at the Clwyd sites. This was further validated with the historical HMS data, which showed lower stream pH at Cwmllanerch than at St Asaph (Figure 4). The two Conwy sites also happen to have the highest percentage of Acid Grassland area, over 35%, draining toward them (Figure 6). Across the Conwy and Clwyd catchments, pH levels showed a positive correlation with the percentage of GAL in the upland draining areas (Table 8). This finding is in contrast with previous studies that have shown that long-term application of fertilizers and manures can contribute to soil acidification, and that pH decreases as the number of cropping years increase (Meng et al. 2005; Zhao et al. 2009). Although fluctuations in hydrological conditions can influence the variability in pH values (Neal et al. 1990), they do not seem to be an influencing factor in the pH differences between the Conwy and Clwyd sites. In addition to the historical HMS data, our sampling data cover a wide range of hydrological conditions (Table 7). Despite this, the differences in the stream pH between Conwy and Clwyd are significant. We suspect that variations in the underlying geology might also be a contributing factor to our pH observations. Although Permo-Triassic sandstones are the dominant bedrock type in both catchments, some

upland areas of the Clwyd catchment do contain Carboniferous Limestone bedrock, which can potentially help reduce the acidity of stream water (Simpson et al. 1993).

Nitrate concentration levels were higher at all three Clwyd sites compared to the Conwy sites, with nitrate concentration being highest at the sample site with the highest percentage of GAL (Table 3 and Figure 7a). While this does suggest a strong influence of agricultural practices on stream nitrate concentration, the antecedent soil moisture conditions might be able to explain some of the temporal variations in nitrate levels at the Clwyd sites. The summer of 2018 was one of the longest and hottest dry periods that Britain had seen for decades (BBC News 2018). This was then followed by a period of considerably high rainfall throughout North Wales, especially during our sampling period. Nitrate concentration levels were highest at Site 2 CW and Site 3 CW on our first sampling day (Table 3), which occurred soon after the first major hydrological events of the autumn season (Figure 5). The relatively lower nitrate concentrations on subsequent sampling days suggest some influence of the hydrological dilution effect. However, this temporal pattern was not observed at Site 1 CO, Site 2 CO, and Site 1 CW. Overall, the concentrations of nitrate, phosphorus, and ammonium are lower throughout the Conwy and Clwyd catchments in comparison to UK averages (Collins et al. 2012). Phosphorus levels were relatively low apart from at Site 1 CW and Site 3 CW (Table 4). In comparison to nitrate, lower phosphorus concentration is needed to disrupt river quality and ecosystems (Smith et al. 1999; Withers and Lord 2002). Therefore, even though concentrations are relatively similar, a higher proportion of agricultural land cover can cause more adverse effects on river quality through phosphorus than nitrate, especially since phosphorus inputs directly cause algal blooms and eutrophication (Carpenter 2008). Ammonium levels were consistently low throughout the sampling period at all sites, apart from at Site 3 CW. There was very little correlation with any form of land

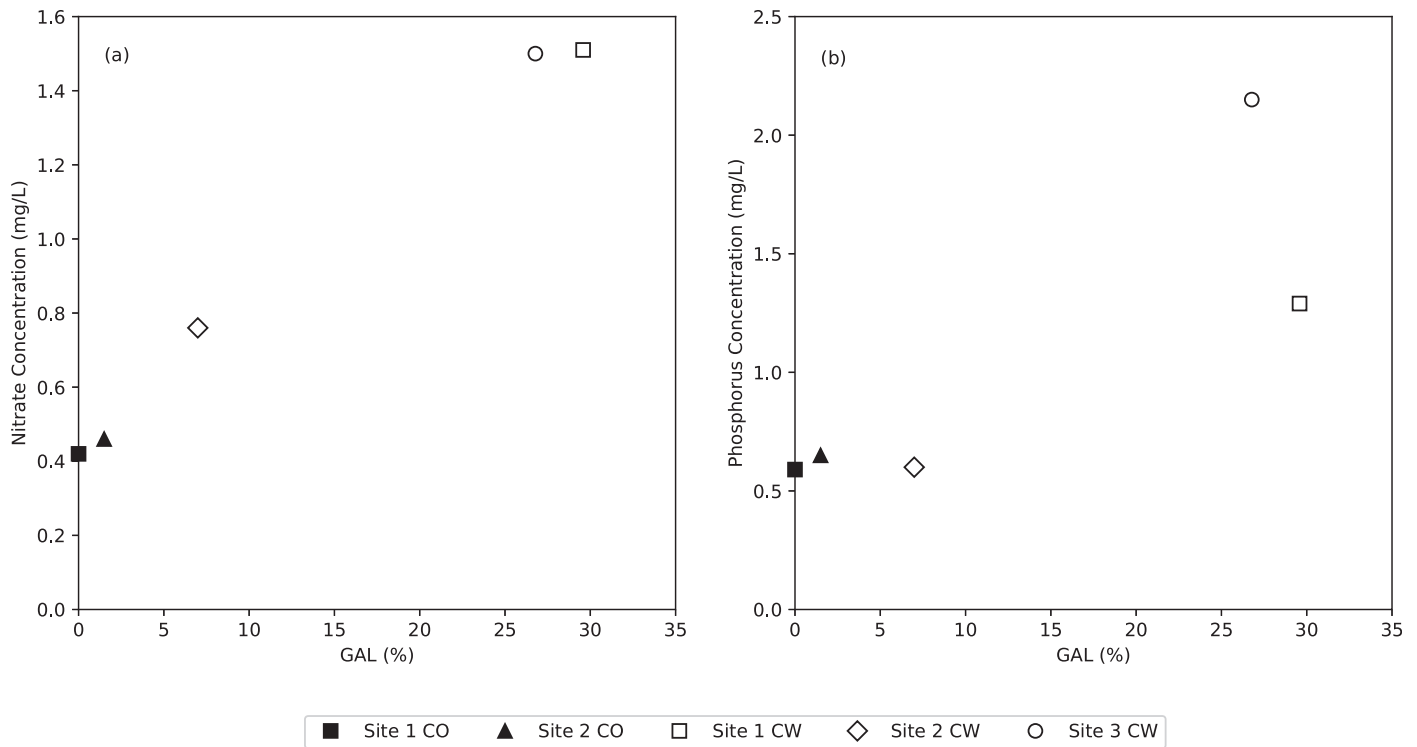


FIGURE 7. Relationship between the proportion of GAL in a catchment and (a) stream nitrate concentration levels, and (b) stream phosphorus concentration levels.

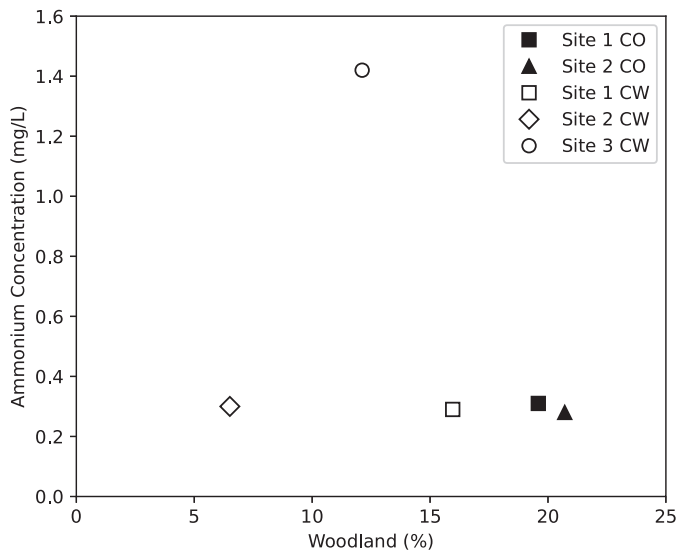


FIGURE 8. Relationship between the proportion of Woodland land cover in a catchment and stream ammonium concentration levels.

cover within the upstream land areas, suggesting that land cover does not influence ammonium concentration within the studied catchments. However, the process of nitrification throughout the watercourse could be converting ammonium to nitrate (Debels et al. 2005) and influencing the levels of nitrate in our study catchments.

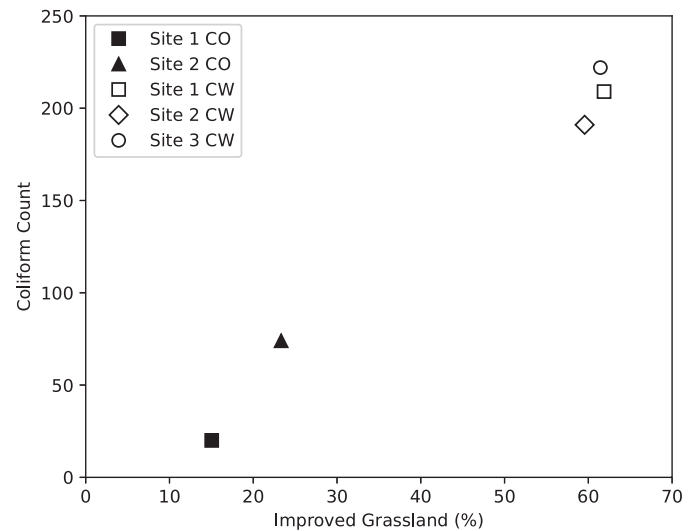


FIGURE 9. Relationship between the proportion of Improved Grassland land cover in a catchment and bacterial coliform count in the stream.

Results obtained from our sampling sites show that the Conwy sites had <80 bacterial coliforms per sample on average, whereas the Clwyd sites had consistently high average coliform counts of over 190 (Table 6). Although both Improved Grassland and GAL showed a positive correlation with coliform count, the Improved Grassland land cover seems to

be a stronger explanatory variable for our observations. This is because Site 2 CW has a much smaller proportion of GAL, compared to the other two Clwyd sites, but still has a high coliform count. In contrast, a comparison of Improved Grassland with the coliform count (Figure 9) clearly distinguishes the Conwy and Clwyd sites. The most likely reason could be the higher intensity of livestock farming in catchments with more Improved Grassland land cover. Intensive agricultural enterprises, especially dairying, are far more prevalent in the Clwyd catchment compared to Conwy. Livestock farming is generally associated with higher fecal contamination of watercourses due to exposed drainage areas or via surface runoff (Edwards et al. 2008). It is difficult to assess with confidence whether septic tanks, one of the highest contributors to the overall coliform count, within agricultural land use also had a direct link to the fecal coliform count. Yet there is a possibility of more septic tanks in the Clwyd catchment due to a higher percentage of intensive agricultural land and rural population than in Conwy. Failing septic tanks have been proven to directly input bacterial coliforms into the surrounding soil and water (Whitlock et al. 2002; Schwab 2007), and therefore could be another potential source of high bacterial coliform count observed over the entire sampling period in the Clwyd catchment.

Although land use can be presumed to have a direct causal link with the presence of bacterial coliforms, hydroclimatic variations can heighten the extent of this pollution. Bacterial coliform count was the highest at all our sampling sites, except Site 3 CW, on 11th November 2018 (Table 6), which also happened to be the sampling day with the highest streamflow values (Table 7 and Figure 5). In recent years, there have been more extended dry periods followed by heavy rainfall events in the United Kingdom, thus resulting in increased surface runoff into the nearby watercourse (Williams et al. 2012). In 2014, the Centre for Environment, Fisheries and Aquaculture Science released a report (Cefas 2014) on the Conwy that concluded that the source of *E. coli* O157 contamination in the catchment was predominately sewage discharge, next to pumping stations or overflows. Since the release of this report, Welsh Water (the regional water provider) have made conscious efforts to improve their wastewater treatment sites. Conwy freshwater is a priority due to the mussel industry that is situated in the Conwy Estuary. Yet the Clwyd catchment, with considerably higher levels of bacterial coliforms, is more influenced by land use due to a higher proportion of land devoted to intensive livestock farming. When discussing *E. coli* O157

specifically, the Williams et al. (2012) study showed that microbial activity differed due to three factors: land use change, competition from background microbes, and the availability of nutrients to sustain the bacteria. This suggests that land use does affect water quality in terms of bacterial coliforms to a large extent, but it is not the only contributor.

CONCLUSIONS

In this study, we sought to quantify the link between land use land cover and stream water quality across two large rural catchments in North Wales, UK. Water quality indicators included pH, EC, nitrate, phosphorus, and ammonium concentrations, and bacterial coliform count. Our results showed clear links between land use land cover and several water quality variables. Importantly, we showed that the dominance of poorer quality agricultural land in a catchment, such as Conwy, correlates with lower levels of all the measured water quality indicators. This suggests that a lack, or lower proportion, of intensively managed agricultural land leads to a higher water quality in rural catchments. Clwyd catchment does contain more high-grade agricultural land than Conwy but is still not dominated by it; no Clwyd site has more than 30% of GAL. Still, the water quality at our three Clwyd sampling sites was significantly poorer than the Conwy sites, especially with respect to nitrate and phosphorus concentrations and bacterial coliform count. Overall, our results suggest that the proportion of high-quality agricultural land within the catchment is a reliable indicator of stream water quality in rural catchments. Lower water quality in these catchments is most likely linked to intensive farming practices. Nonetheless, a finer scale analysis would be required to identify and implement specific pollution control measures for improving the stream water quality. Such an analysis would preferably have to be conducted at the spatial scale of individual farms and within the context of hydrological water quality modeling.

APPENDIX

This appendix contains the areal coverage data of each land cover class in the catchments that drain toward our five sample sites (using LCM 2015, LCM 2007, and pALC classifications).

TABLE A1. LCM 2015 and 2007 land cover classes for Site 1 CO.

Class	2015 area (ha)	% of catchment area (2015)	2007 area (ha)	% of catchment area (2007)
Acid grassland	960	35.82	882	34.36
Bog	341	12.72	401	15.62
Broadleaf woodland	24	0.90	23	0.90
Coniferous woodland	501	18.69	384	14.96
Freshwater	1	0.04	2	0.08
Heather	349	13.02	372	14.49
Heather grassland	36	1.34	172	6.70
Improved grassland	403	15.04	278	10.83
Inland rock	59	2.20	48	1.87
Suburban	6	0.22	5	0.19

TABLE A2. LCM 2015 and 2007 land cover classes for Site 2 CO.

Class	2015 area (ha)	% of catchment area (2015)	2007 area (ha)	% of catchment area (2007)
Acid grassland	13,684.6	36.11	11,978.65	32.07
Arable/horticulture	10.1	0.03	556.27	1.49
Bog	4,124.1	10.88	4,339.57	11.62
Broadleaf woodland	2,195.8	5.79	1,293.10	3.46
Coniferous woodland	5,654.2	14.92	5,093.87	13.64
Freshwater	180.6	0.48	182.32	0.49
Heather	2,054.5	5.42	1,579.73	4.23
Heather grassland	839.7	2.22	4,661.26	12.48
Improved grassland	8,843.3	23.33	7,286.35	19.51
Inland rock	158.8	0.42	176.62	0.47
Suburban	150.7	0.40	174.40	0.47
Urban	3.1	0.01	31.92	0.09

TABLE A3. LCM 2015 and 2007 land cover classes for Site 1 CW.

Class	2015 area (ha)	% of catchment area (2015)	2007 area (ha)	% of catchment area (2007)
Acid grassland	1,837	13.44	1,290.11	9.44
Arable/horticulture	547.1	4	1,890.30	13.83
Bog	0.03	0.0002	0.00	0.00
Broadleaf woodland	1,059.5	7.75	1,066.42	7.80
Calcareous grassland	11.9	0.09	18.62	0.14
Coniferous woodland	1,121.8	8.21	1,107.52	8.11
Freshwater	5.7	0.04	7.76	0.06
Heather	217.4	1.59	251.23	1.84
Heather grassland	19.3	0.14	165.28	1.21
Improved grassland	8,455	61.88	7,543.62	55.21
Inland rock	20.8	0.15	16.42	0.12
Neutral grassland	47.8	0.35	61.70	0.45
Suburban	258.6	1.89	183.78	1.34
Urban	62	0.45	61.48	0.45

TABLE A4. LCM 2015 and 2007 land cover classes for Site 2 CW.

Class	2015 area (ha)	% of catchment area (2015)	2007 area (ha)	% of catchment area (2007)
Acid grassland	4,600	23.89	4,464.89	23.19
Arable/horticulture	36.2	0.19	883.58	4.59
Bog	922.9	4.79	419.19	2.18
Broadleaf woodland	870	4.52	860.93	4.47
Coniferous woodland	383.4	1.99	333.19	1.73
Freshwater	81.4	0.42	85.95	0.45
Heather	776.6	4.03	163.76	0.85
Heather grassland	16.6	0.09	759.57	3.95
Improved grassland	11,466	59.56	11,183	58.09
Inland rock	40.4	0.21	35.08	0.18
Suburban	50.5	0.26	54.65	0.28
Urban	7.9	0.04	7.81	0.04

TABLE A5. LCM 2015 and 2007 land cover classes for Site 3 CW.

Class	2015 area (ha)	% of catchment area (2015)	2007 area (ha)	% of catchment area (2007)
Acid grassland	11,933.8	16.33	4,144.42	7.70
Arable/horticulture	2,937.6	4.02	9,873.20	18.35
Bog	922.9	1.26	1.48	0.00
Broadleaf Woodland	4,911.3	6.72	4,547.96	8.45
Calcareous grassland	128.6	0.18	0.00	0.00
Coniferous woodland	3,942.7	5.40	3,221.72	5.99
Freshwater	115	0.16	35.59	0.07
Heather	1,392	1.91	665.45	1.24
Heather grassland	52.2	0.07	594.96	1.11
Improved grassland	44,896	61.44	29,312.92	54.47
Inland rock	228.5	0.31	113.84	0.21
Neutral grassland	263.6	0.36	436.40	0.81
Saltmarsh	3.9	0.005	0.00	0.00
Suburban	1,041	1.42	664.60	1.23
Supralittoral sediment	3.2	0.004	0.00	0.00
Urban	295.7	0.40	202.56	0.38

TABLE A6. pALC land cover classes for Site 1 CO. Proportion of GAL = 0%, PAL = 88.7%.

Class	Area (ha)	% of catchment area
Grade 4	29.15	4.05
Grade 5	610	84.65
Nonagricultural	81.44	11.30

TABLE A8. pALC land cover classes for Site 1 CW. Proportion of GAL = 29.6%, PAL = 20.5%.

Class	Area (ha)	% of catchment area
Grade 1	871.5	6.38
Grade 2	1,331.7	9.75
Grade 3a	1,837.3	13.45
Grade 3b	4,453.9	32.59
Grade 4	2,189	16.02
Grade 5	606.3	4.44
Nonagricultural	2,158.3	15.79
Urban	216.5	1.58

TABLE A7. pALC land cover classes for Site 2 CO. Proportion of GAL = 1.5%, PAL = 77.9%.

Class	Area (ha)	% of catchment area
Grade 3a	567.6	1.50
Grade 3b	581.9	1.54
Grade 4	7,134.4	18.82
Grade 5	22,392.8	59.08
Nonagricultural	7,108.9	18.76
Urban	114.1	0.30

TABLE A9. pALC land cover classes for Site 2 CW. Proportion of GAL = 7%, PAL = 52.9%.

Class	Area (ha)	% of catchment area
Grade 2	518.2	2.69
Grade 3a	828.3	4.30
Grade 3b	6,465.9	33.58
Grade 4	4,928	25.60
Grade 5	5,252.8	27.28
Nonagricultural	1,259.7	6.54

TABLE A10. pALC land cover classes for Site 3 CW. Proportion of GAL = 26.8%, PAL = 29.7%.

Class	Area (ha)	% of catchment area
Grade 1	2,628	3.60
Grade 2	5,963	8.16
Grade 3a	10,973.3	15.02
Grade 3b	22,477.7	30.76
Grade 4	13,765.3	18.84
Grade 5	7,905.5	10.82
Nonagricultural	8,589.3	11.75
Urban	767.6	1.05

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AUTHORS' CONTRIBUTIONS

Elizabeth C. Crooks: Conceptualization; data curation; formal analysis; investigation; methodology; validation; visualization; writing — original draft; writing — review and editing. **Ian M. Harris:** Investigation; resources; software; visualization; writing — review and editing. **Sopan D. Patil:** Conceptualization; formal analysis; investigation; supervision; visualization; writing — review and editing.

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